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To cite this article: A Masih and A P Sergeev 2018 *IOP Conf. Ser.: Earth Environ. Sci.* **167** 012023

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Heavy Metal Contamination Assessment in Near Surface Soils: A Case Study from Subarctic Region of Russia

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Abstract: Under the initiative of a routine ecological screening taken by the Russian state territories, soil surface assessment of heavy metals such as Cr, Cu, Ni, Mn, etc. was conducted in a city called Noyabrsk located in a subarctic region of Yamalo-Nenets Autonomous Okrug (YNAO) Russia. During survey a total of 321 soil samples were collected from different parts of the region including residential (237 samples), industrial (80 samples) and from background locations (4 samples) of the city. In order to determine the general ecological conditions of the area chemical analysis was conducted. Geostatistical tools along with other statistical techniques have been adopted to explore, analyse and map the obtained concentrations of the heavy metals. Results drawn have revealed some moderate – high anomalies of As, Cr and oil concentrations in industrial as well as in residential regions that can be a threat to public health. The aim of the paper is to assess the pollution status of urban soil and discuss the soil contamination sources for the future planning and management of Noyabrsk city.

1. Introduction

Heavy metal assessment is an important part of state's responsibilities because it ensures the environmental safety of its residents. It also brings sagacity of investigating the prime emission sources of heavy metals as their impact on the surrounding environment can be significant. Various studies have been conducted on soil pollution as a result of numerous industrial activities in many parts of the World, however there are very few investigations to author's knowledge that have been made in subarctic region of Russia assessing the ecological conditions of urban areas for pollution risk. Essential environmental components such as soil, biota, snow, bottom sediments, etc. are generally the places of accumulation for pollutants from different sources, therefore, surfaces containing pollutants are possibly be the best sources to investigate the nature and characteristics of the pollution [1], [2]. Soil ecological screening is vital because the composition of soils are intervened most of the times by rocks, water and air [3]. These interventions get deposited in the form of soil layers which preserve pollutants record in it for decades either carried by sediments, water, and air or caused by anthropogenic activities. The chemical variability of the parent rock or soils should be considered while determining the origin of the soil surface contamination [3]. Field data gathered mainly depend on the type and intensity of emission source as well as on other factors such as hydrological and meteorological conditions and climatic variabilities [3]. Such irregularities while collecting data sometimes lead to spatial heterogeneity that can seriously affect the anomalies generated due to tainted data to predict the environmental pollution.

Interpolation a geostatistical tool has extensively been used in recent years in soil pollution estimation. It performs the pollution assessment to study the spatial variations and ensures the certainty of its estimates. Moreover it evaluates spatial pattern and distribution of pollutants and enables spatial



mapping [4]. Recent geostatistical studies [3], [5] have focused on urban soils and have discussed the usefulness of adopting interpolation techniques to address spatial pattern and uncertainties in soil concentration data.

The paper discusses near surface heavy metal contamination in subarctic region of Russia. Spatial interpolation is the main method employed assessing the heavy metal pollution in area by using ordinary and indicator kriging maps presenting the concentrations of heavy metals in the study area.

2. Material and methods

The study conducted was a part of a routine ecological screening survey structured by the authorities of the YNAO in August 2006. Noyabrsk is the largest city in the southern YNAO district located in the middle of arctic zone of Western Siberian plains covering an area of 38.84 square kilometres as shown in Figure 1. The local urban soils are mainly consist of illuvial-humus podzol with little content of organic components [3], [6] whereas its composition is 100% sand. The economy of the region majorly based on hydrocarbon production with a fact that the place has always considered home ground to one of the biggest oil and gas company “Gazprom”. Due to the fact the major pollutants in the urban soils were expected to be phenol and mineral oil against the other high concentrations of heavy metals revealed such as Arsenic and Chromium.



Figure 1. Location map of the study area

During the survey according to the extent of the region a total of 321 soil samples of different spatial scales on a squared-grid sampling scheme at a depth 0-5cm were collected from residential, industrial and background locations (typically acquired to compare values) of the city. An increased sampling interval in the industrial zone was adopted in comparison with the samples collected from residential area. At each point, 5 soil samples were taken, 4 of which making a square geometry of side 1m around the 5th located in the middle. Geographical coordinates of each sampling point were recorded using GPS, and thereafter soil samples were stored in polythene bags each weighed about 1.5kg prior to chemical analysis. Preparation of all samples and their chemical analyses with the type of methods employed in laboratory have already been discussed in detail in our previous work [1]. Chemical analysis was aimed at determining the hydrogen ion exponents of the following agents with the soluble form of F, Cr, Co, Ni, Cu, Zn, and the total form of Al, Cr, Mn, Fe, Co, Cu, Ni, Zn, As, Cd, Sb, Hg, Pb, phenol and oil concentrations in the topsoil.

Geostatistical tool of variography was employed to analyse and interpret the data, generally based on a theory of localize variable distributed in space showing a spatial correlation such that closer the samples higher the correlation and vice versa [7]. Variography is used to measure the spatial variability and dependency of a regionalized variable by calculating variogram/semi-variogram. It provides the input information for the spatial interpolation. The variogram function is expressed as:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} (Z(x_i) - Z(x_i + h))^2$$

where $\gamma(h)$ is the semivariance (variogram), $Z(x_i)$ is the value of the variable Z at location of x_i , and $N(h)$ is the number of pairs of samples separated by the lag distance h .

Information generated through variography was used to calculate sample weighting factors for spatial interpolation by ordinary and indicator kriging.

The anisotropic spatial variability was also considered in accordance with the symmetrical property of variogram function for all significant variables. Concerning the modelling of experimental variograms to get the information about the spatial structure and input parameters for kriging, different models i.e. exponential and Gaussian models were employed. The information acquired was later used for calculating weighting factors for spatial interpolation by the ordinary and indicator kriging.

The obtained concentration of Cr, As and oil are mapped and interpreted using Geostatistical Analyst tool in ESRI ArcGIS software with ordinary and indicator kriging as interpolation techniques. Other routine statistical analyses such as probability distributions and Spearman rank correlation coefficients were performed by using Statistica software.

3. Results and discussion

The ministry of Natural Resources and Ecology of Russian Federation controls the total content of nine heavy metals [8]. There are different types of approaches used in Russia as permissible standards such as maximum permissible concentrations (MPC), others include provisional permissible concentrations (PPC) and background values comparison when there are no standards considered for the concentrations estimated. In Noyabrsk soil data set, for metalloid Arsenic (As) both MPC and PPC approaches were considered, Chromium (Cr) values were compared with the standards set by PPC and also with the world soil standards as well, whereas for oil concentrations background location values were estimated.

Table 1. Descriptive statistics of heavy metals in study area.

Elements	Mean	Median	Minimum	Maximum	Std.Dev.	Coef.Var.	Skewness
Al	11210.7	10270	101	32940	4764.8	0.43	1.27
Cr	64.56	61.41	16.57	140	22.81	0.35	0.74
Mn	141.63	130.45	61.81	529.1	54.21	0.38	3.4
Fe	13220.05	12785	101.	28270	4000.2	0.3	0.6
Co	4.69	4.26	2.00	101	5.589	1.19	16.25
Ni	11.76	11.01	3.58	101	6.652	0.57	8.18
Cu	18.85	14.67	5.01	341.49	25.3	1.34	9.29
Zn	17.31	14.14	5	133.63	12.5	0.73	4.14
As	1.6	1.42	0.14	5.2	0.79	0.51	0.96
Pb	6.33	4.56	1	120.01	10.09	1.59	7.99
Oil	24.48	6.88	0.93	829.4	75.13	3.07	7.51

The statistical summary of the data set for heavy metals with other soil variables including oil is given in Table 1. Interestingly, almost all chemical elements assessed were fallen within the permissible concentration limits set under the environmental law of Russia, expect, the arithmetic mean value for oil concentrations which is very high as compared to its median values with high skewness, confirming some high anomalies in the study area. It is to be noted that the mean value for the concentration of oil in the topsoil is 4-times higher than the median value. The concentration of oil has ranged from 0.93 to 829.40mg/kg with a mean value of 24.48mg/kg. Also the mean value for oil calculated separately for industrial zone (37.66mg/kg) was almost 2-times higher than residential

zones (19.7mg/kg), while both are way higher than the average value (2.50mg/kg) of 4 background location concentrations collected.

The general toxicological GOST 17.4.1.02-83 operated in Russia divides heavy metals/metalloids into three classes based on the degree of hazardousness, according to which Arsenic makes into the list of elements considered the most hazardous with other elements include Cd, Hg, Se, Pb, Zn [9]. In Table 1, the mean value of As (1.6mg/kg) is slightly higher than its median value, which is nearly equal to the permissible limits set under MPC and PPC i.e. 2mg/kg for the land with composition sand or loamy sand [10] by the Russian Federation. The As metal concentrations in studied area showed that around 90 sample points i.e. 30% of the total sampling points of As concentrations were higher than the strict soil guidelines set for As by MPC and PPC.

Chromium (Cr) currently categorized in the moderately hazardous element class according to toxicological GOST. Table 1 shows that the mean value of Cr is 64.56mg/kg which is slightly higher than its median value with average skewness can join oil and As in the list of elements that can be a threat to public health due to its high concentration values in study area. The average concentration of Cr appeared in the selected region falls within the reference value set under environmental law with only few Cr sample points crossing the Russia's permissible clarke limit of 122mg/kg [11], [12]. However, in an international perspective the distribution of the Cr in study area still remains a point of interest, because the permissible chromium clarke in world soils is 59.5 mg/kg [11], [13]. Keeping that as a reference value, only 38% sample points in our case had a Cr concentration less than the guideline set for world soils whereas the remaining 62% have surpassed the reference value.

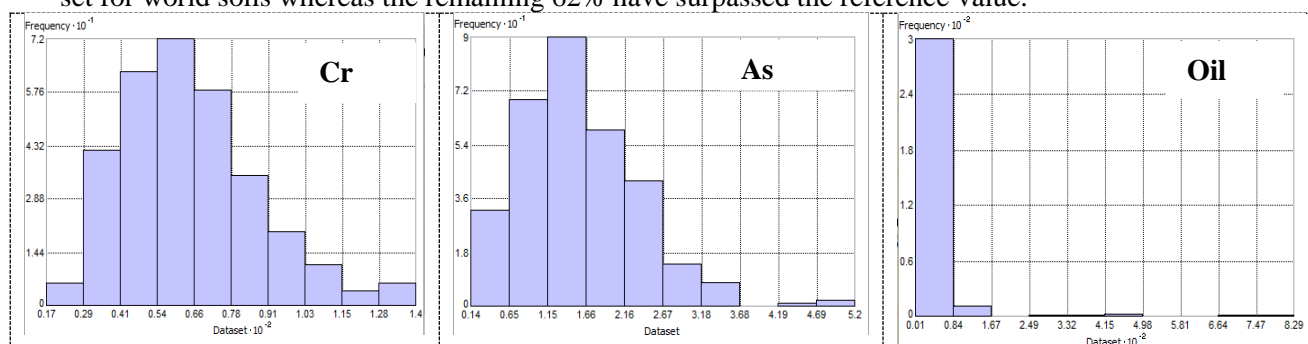


Figure 2: Frequency distribution for Chromium, Arsenic and Oil

Table 2. Spearman Rank Correlation.

	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Pb	Oil
Al	1.0										
Cr	-0.02	1.00									
Mn	0.39	0.51	1.00								
Fe	0.13	0.78	0.65	1.00							
Co	0.06	0.58	0.56	0.57	1.00						
Ni	-0.05	0.71	0.55	0.7	0.66	1.00					
Cu	-0.18	0.75	0.45	0.72	0.54	0.78	1.00				
Zn	0.30	0.05	0.35	0.08	0.20	0.30	0.11	1.00			
As	0.23	0.27	0.39	0.38	0.29	0.25	0.25	0.09	1.00		
Pb	0.35	0.09	0.21	-0.09	0.03	0.18	0.06	0.54	0.09	1.00	
Oil	-0.09	-0.01	0.05	-0.08	0.16	0.30	0.09	0.48	-0.13	0.36	1.00

*Highlighted numbers are significant at $P < 0.05$

According to Table 1 and Figure 2 the distribution of oil concentrations in Noyabrsk topsoil is highly positively skewed in comparison with the moderately skewed and way normally distributed concentration values of As and Cr. The coefficient of skewness of Cr, As and oil clarkes distributions were computed using Kolmogorove-Smirnov test, knowing to the fact that normal distribution is

required in linear geostatistics [14], because abnormal distribution can sometimes seriously affect the kriging results. Coefficient of variation (CV) values calculated for the data set suggested that among As, Cr and oil concentrations, oil showed the greater variation against the two metals.

Not all heavy metals entering surface soil are considered pollutants. Therefore, to get more insight into data acquired, Spearman Rank Correlation was performed at $P < 0.05$ to investigate the relationship among elements (Table 2). Chromium (Cr) presented a strong positive correlation with Mn, Fe, Co, Ni, Cu, and As. There existed no significant correlation between oil concentrations and Cr according to Table 2, rather it showed a negative correlation with As, which suggest that the concentration values of Cr and As are most probably not sourced by the high consumption of oil in the industrial zones of the city, however the strong correlation of Cr and As with one another as well as with the top half of the elements presented in Table 2, indicates the presence of single emission source.

3.1. Geostatistical and anisotropy analysis

To make better decisions variography analysis has been performed using topsoil parameters. Also for creating surfaces the data was thoroughly explored for obvious errors that can drastically affect the output prediction surfaces. Before creating surfaces, distribution of data was examined, global trends were identified and removed, and spatial autocorrelation and directional influences were understood in Geostatistical Analyst. Before picking the best model experimental variograms were tested with different theoretical models such as Spherical/Gaussian/Exponential functions and their results were compared. The selection criteria of each model was based on which best fitted to experimental variogram behaviour (table 3).

Table 3: Experimental variograms

Variable	Model	Nugget	Sill	Spatial Dependency
Cr	Exponential	326.6	575.9	Moderate
As	Exponential	0.13	0.63	Strong
Oil	Gaussian	3.2	3202.8	Strong

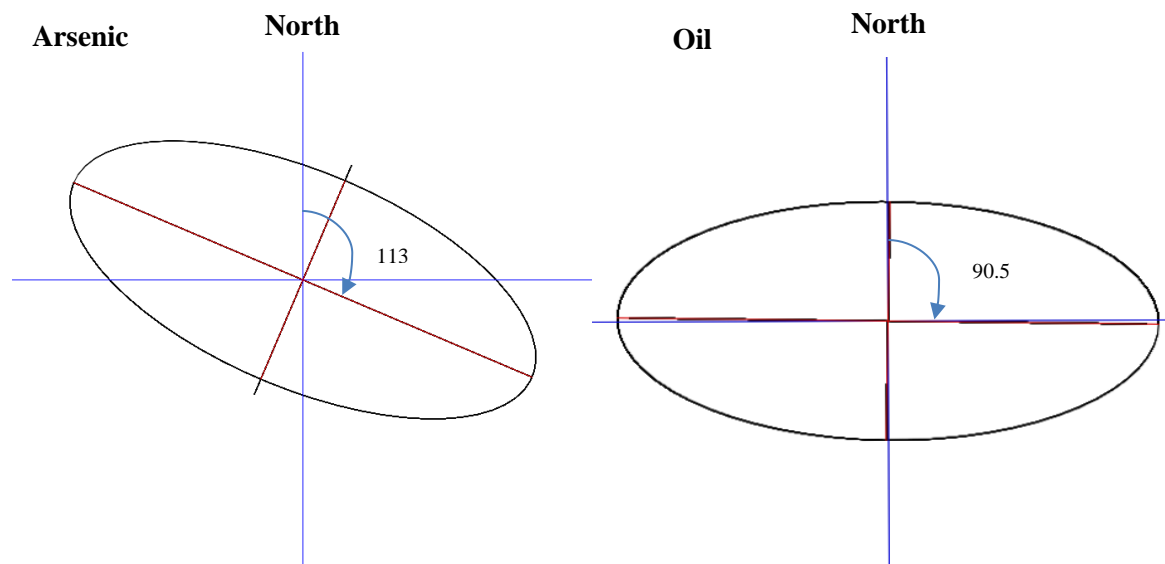
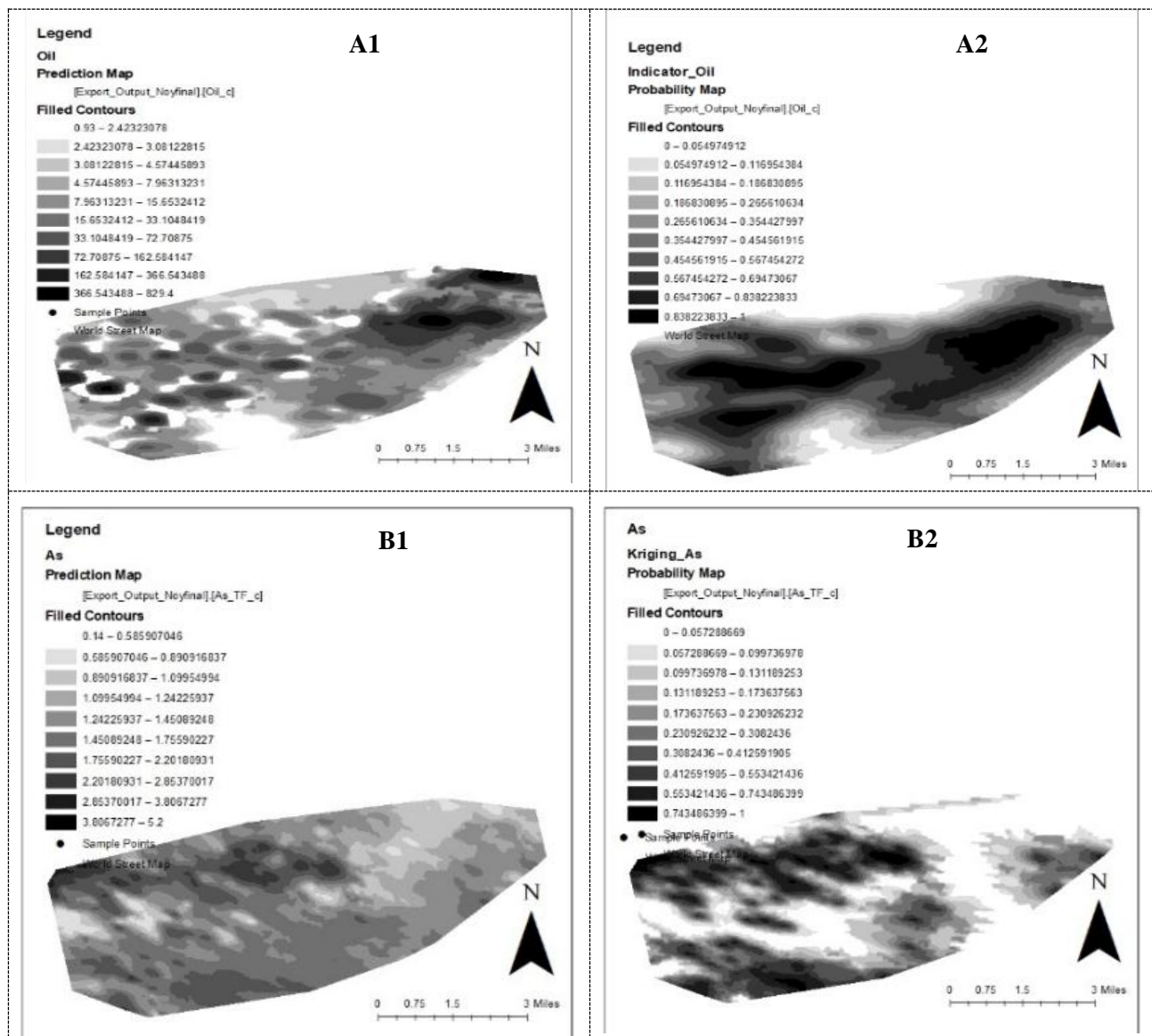


Figure 3. Anisotropic effect for As and Oil estimated clockwise from North by using geostatistical analyst determines their distribution along major axis with perpendicular minor axis.

For to the degree of spatial dependency the work by Cambardella [15] is followed, according to which if the ratio of nugget to sill multiplied by 100 is less than 25% then the variable is considered strongly spatially dependent, if the ratio ranges from 25% to 75% the variable is moderately spatially dependent and in case the ratio crosses 75% then data is weakly spatially dependent.

Following the rule, the experimental variograms of As and Oil concentrations appeared to be strongly spatially dependent in comparison with moderately spatially dependent variogram of Cr. The anisotropic effect of elements shown in figure 3 clearly separates oil from As anomaly that could have been the possible emission source due to its minimum presence in industrial zones. Anisotropic analysis represents that the major oil anomaly appeared in study area is mainly distributed along E-W direction making a right angle with North, whereas residential region bounded As anomaly lies in NW-SE direction (Figure 3).



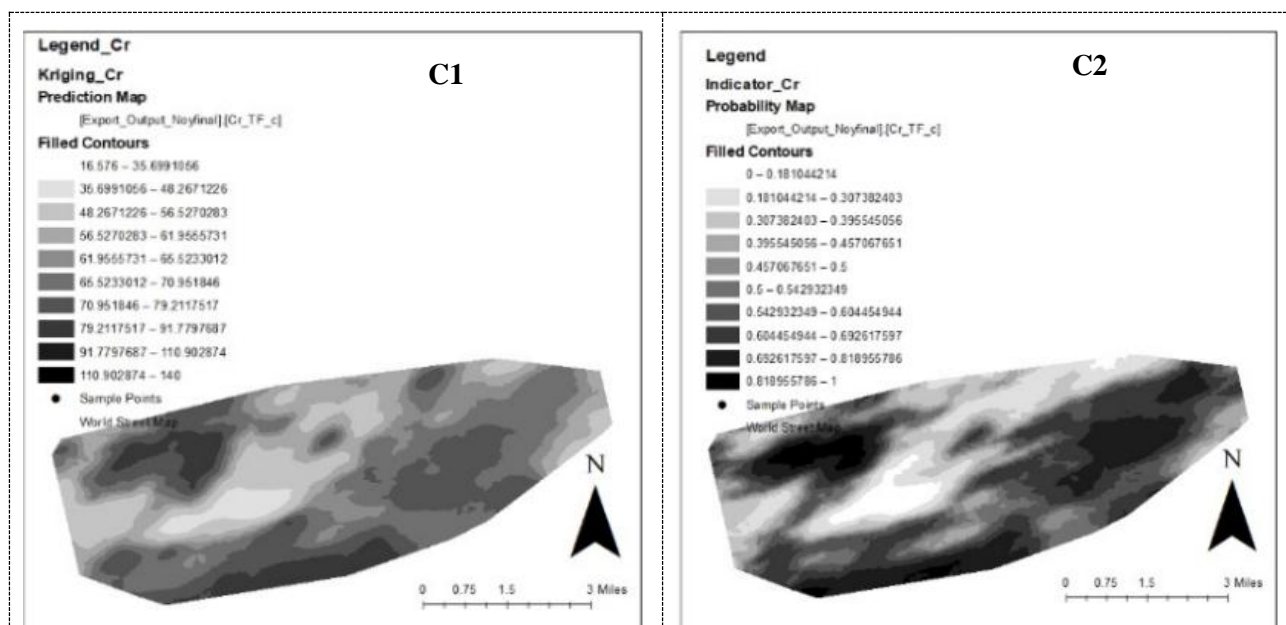


Figure 4. Kriged maps of oil, As, Cr (A1, B1, C1) clarkes using ordinary kriging and probability maps for the estimated concentrations (mg kg⁻¹) of oil, As, Cr (A2, B2, C2) using Indicator kriging.

To precisely mark the probable polluted zones that have violated the guidelines set by the State, the indicator kriging technique adopted requires a threshold value for each element—oil, As and Cr. The threshold values assigned to; oil concentrations are compared with background values, Arsenic was assigned value set by MPC and PPC, and Cr has been compared with its median value (61.41mg/kg) which is nearly equal to reference guide set for world soils. It is quite obvious in Figure 4 that the concentration of oil is significant in industrial zones with its few major spots in residential zone, whereas the high concentrations of As rather appeared in settlement zones. On contrary, kriged map of Cr have shown a parallel existence in both residential and industrial regions, however, its anomaly in residential area is comparatively higher than in the industrial zone of the city. Furthermore, the kriged maps confirm the correlation between oil, As and Cr (Table 2) i.e. the association of both metals – As and Cr with oil is either negative or not significant to be correlated. Moreover, the absence of As in the industrial zones is evident that the concentration of As metal (most hazardous) in residential is probably not been sourced by industrial activities but perhaps region has been contaminated by human-induced activities in the urban soil.

It wouldn't be justified declaring that the sampling area is polluted, however, a considerable portion i.e.30% of the metalloid (As) the most hazardous to local standards and 62% of Chromium (Cr) values according to international guideline set for world soils have crossed the permissible boundaries which can be a threat to public health, therefore, seek local government intention.

4. Conclusion

The geostatistical approach adopted for the study has examined and interpreted the topsoil heavy metal concentrations in Noyabrsk a city situated in subarctic region of Russia. Although the region is well known for its large amount of hydrocarbon extraction yet surprisingly, almost all chemical elements assessed appeared within the local permissible ecological limits except the moderate anomalies of As, Cr and oil particularly in residential zones. The results drawn indicate that around 30% sampling points of Arsenic a most hazardous and strictly monitored metalloid with a permissible concentrations of just 2mg/kg in Russia, have violated the ecological limits. On the other hand a very few samples of Chromium a heavy metal have surpassed the local reference values, while in an international perspective 62% sampling points of the same metal (Chromium) have violated the limits set for world soils. Although oil clarkes variations revealed in industrial zone of urban topsoil are two-times higher as compared to the settlement zones, however, the study conducted showed that it doesn't share a

strong correlation with the high concentrations of Arsenic and Chromium metals to be the soil contamination source. It seems as anthropogenic activities are possibly the emission source of moderate anomalies of Arsenic and Chromium within settlement region especially, hence responsible of contributing into the urban soil pollution of the city.

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